2015 DOE Vehicle Technologies Office Annual Merit Review

In-Situ Investigation of Microstructural Evolution During Solidification and Heat Treatment in a Die-Cast Magnesium Alloy

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Pacific Northwest National Laboratory

11th June 2015

Project ID: LM092

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Project Overview

Timeline

- Start – Oct. 2013
- Finish – Sept. 2015
- 60% Complete

Budget

- Total project funding:
  - PNNL: $500k

Barriers

- Predictive Modeling Tools: Adequate predictive tools that will enable the low cost manufacturing of lightweight structures would reduce the risk of developing new materials for vehicular applications
  - Microstructural evolution during solidification at high cooling rates is not available to validate existing models

Targets

- The DOE-VT (2011-2015 multi-year plan) target for weight reduction of the vehicle and its subsystems is 50%
  - Understand solidification and heat-treatment kinetics far from equilibrium (AZ91D)

Partners

- Industry participants:
  - ESI

Relevance/Objectives

Relevance

- Development of modeling tools: In situ kinetic information will help develop modeling tools for accurate microstructure prediction of advanced Mg alloy die-castings
- Petroleum displacement: Improved predictive capability will reduce development costs & enable high-volume manufacturing of Mg die-castings
    - Mass-saving potential for Mg castings ~40-60%
    - Fuel economy increase by ~30-40%
    - Year 2010 – US cars consumed ~3.9 Million barrels per day; 20% reduction in gallons/mile → Save ~0.8 Mbpd

Objectives

1. Understand the solidification kinetics of AZ91 melt at high cooling-rates
2. Understand the kinetics of phase evolution of $Mg_{17}Al_{12}$ and α-Mg during heat-treatment

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Technical Barriers

- Experimental technique to study in-situ solidification kinetics at “high” cooling rates (100-1000 ºC/s) does not exist
  - Conventional approach: Post-mortem (e.g. using chills, followed by microhardness, mechanical property measurements)
  - In-situ neutron diffraction and thermal analysis → 0.5 ºC/s
  - DSC cooling rates → Max. 50 ºC/min. (<1 ºC/s)
  - Dilatometers → ~200 ºC/s (not applicable to melting-solidification)
  - Current solidification models are based on local equilibrium at liquid/solid interface which may not be the case under high cooling rates of HPDC

Knowledge Gap: Microstructural evolution during solidification at high cooling rates is not available to validate existing models

Project Milestones & Deliverables

Year	Milestone/ Deliverable	Description	Due	Status
Year I	**Milestone #1**	**Setup a sub-contract with ESI North America (ESI NA)**	**12/13**	✓
	Milestone #2	**Develop procedures to sputter coat AZ91 as a think film, up to 100 nm thick, for in-situ experiments**	**03/14**	✓
	Milestone #3	**Determine optimal laser power and pulse-width to locally melt the AZ91 sample just above its melting point**	**06/14**	✓
	Milestone #4	**Acquire 10 diffraction patterns of Mg-Al and $Mg_{17}Al_{12}$ at a cooling rate between 100-1000 ºC/s during solidification of molten AZ91 in the DTEM** -Provide NIST with 10 diffraction pattern data files of Mg-Al and $Mg_{17}Al_{12}$ formed during solidification of molten AZ91	**09/14**	**Postponed**
Year II	**Milestone #5**	**Simulate as-cast AZ91D microstructure at 3 cooling rates between 1-1000 ºC/s**	**12/14**	✓
	Milestone #6	**Quantify liquid/solid front velocity in AZ91 at a die-casting cooling rate**	**03/15**	**Postponed**
	Milestone #7	**Model Mg/$Mg_{17}Al_{12}$ interface stability & diffusivities of vacancies and defects in $Mg_{17}Al_{12}$**	**06/15**	**On-track**
	Milestone #8	**Measure evolution kinetics of ($Mg_{17}Al_{12}$) β-phase in die-cast AZ91 for isothermal aging between 150-300ºC**	**09/15**	**On-track**

Technical Approach

	Experimental	Modeling
Solidification	Develop in-situ melting/solidification technique inside an electron microscope for imaging the solidification of Mg alloys	Correlate experimental data with predictions from commercial solidification software (ProCAST) and to determine validity of the code for HPDC Mg alloys
Heat-treatment	Develop in-situ heat-treatment approach to study kinetics of phase evolution in as-cast microstructure	Perform atomistic simulations to understand microstructural evolution in non-equilibrium microstructure

AZ91

(Applicable to other Mg alloys as well)

Project Tasks

Task 1: Project Management

Task 2: Determination of in-situ solidification kinetics

- DTEM sample fabrication
- DTEM in-situ solidification characterization

Task 3: Determination of in-situ kinetics during heat-treatment

- Specimen fabrication for STEM
- In-situ heat-treatment & characterization

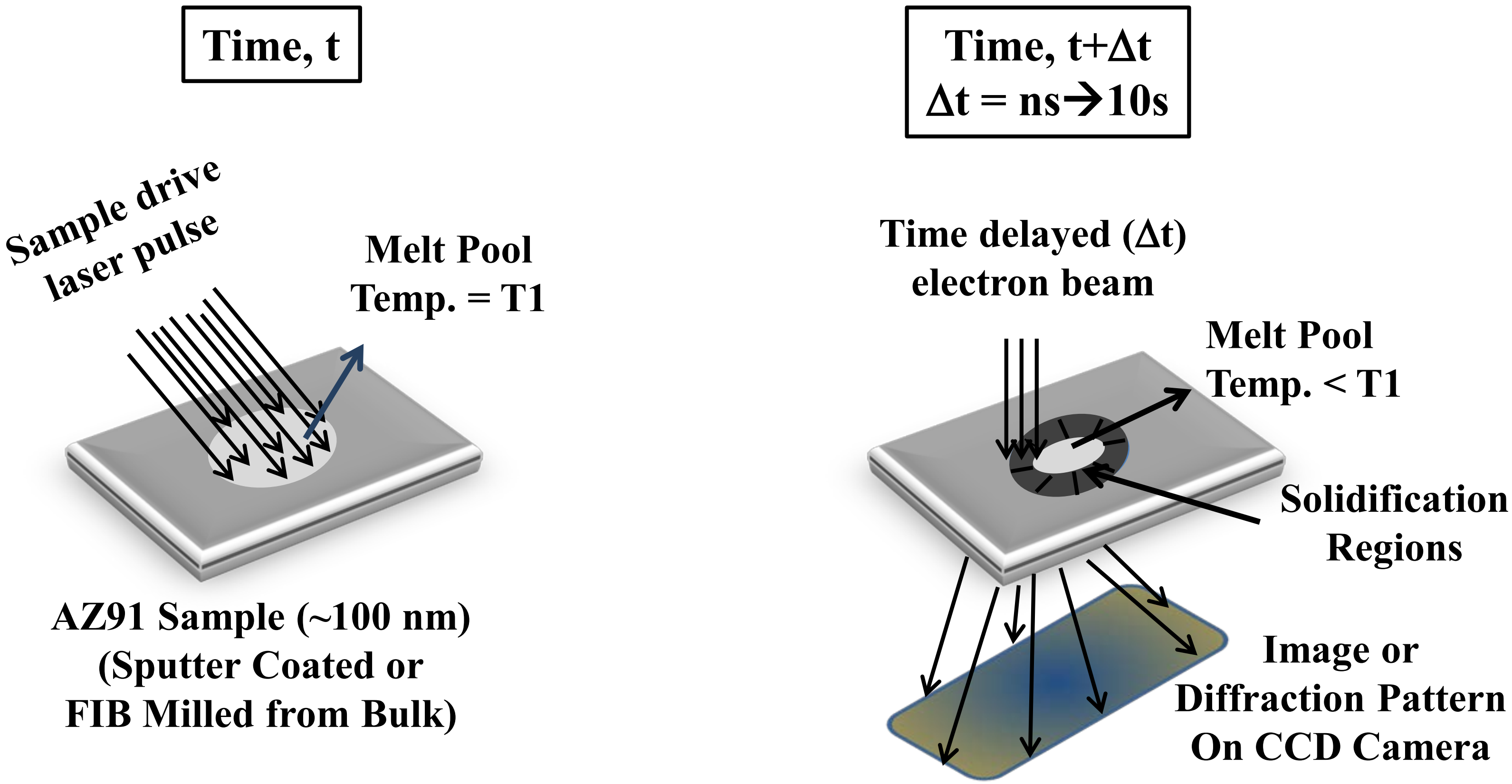
Task 4: Solidification Modeling

- Back-diffusion thermodynamics calculations
- Microstructure prediction calculations

Task 5: First-principles Atomistic Modeling

- Structural property calculation of α-Mg and $Mg_{17}Al_{12}$ phases
- Effect of defects and vacancies

Background:
In-situ Solidification Kinetics Concept



- Nucleation/growth kinetics
- Phase volume fractions
- Velocity of solid/liquid interface

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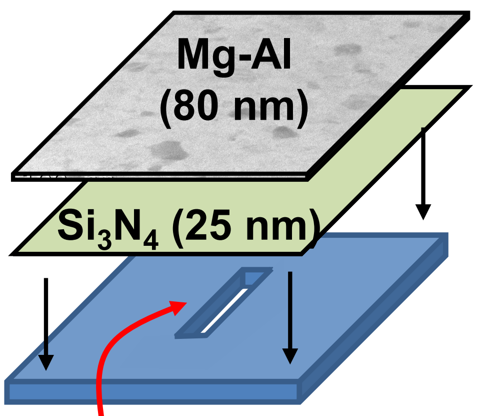
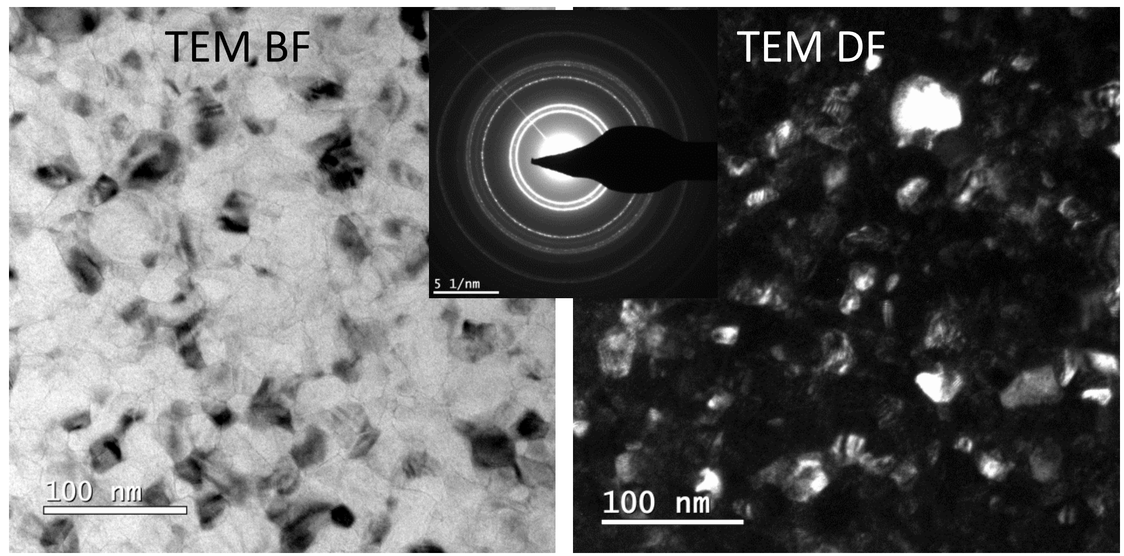
Technical Accomplishments:
DTEM Sample Fabrication

Specimen Requirements

- Electron transparent
- Uniform composition
- Self-contained melt pool
- Min. size 10 μm x 10 μm



Si Chip with window (400 μm x 30 μm)



Element	Weight %	Atomic %	Uncert. %
Mg(K)	90.7	91.55	1.14
Al(K)	9.29	8.44	0.38

- Sputtered films with Mg-9 wt.% Al
- Nanocrystalline (~14 nm)

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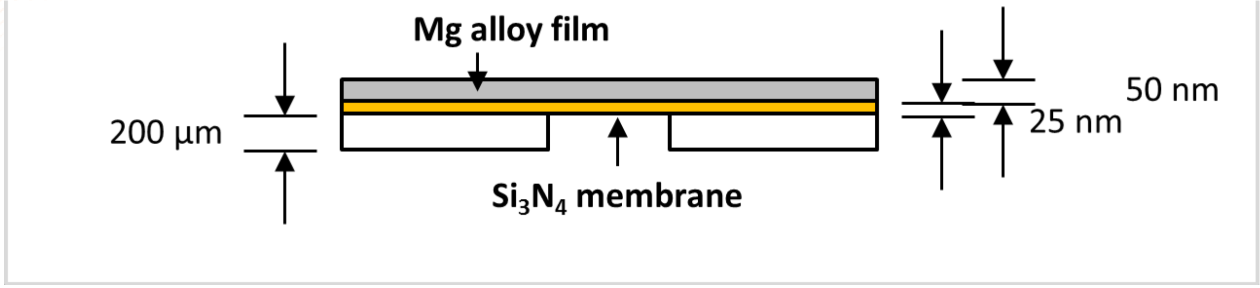
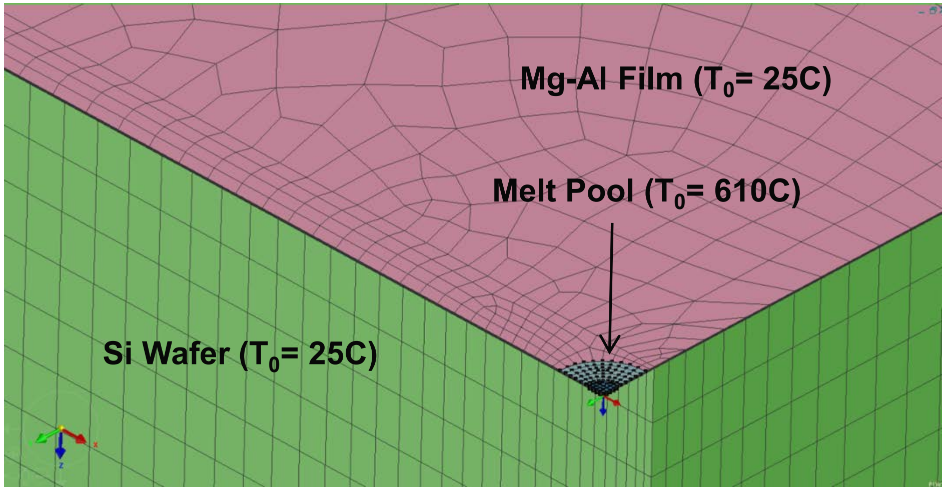
Technical Accomplishments:
Thermal Modeling (in-situ melting)

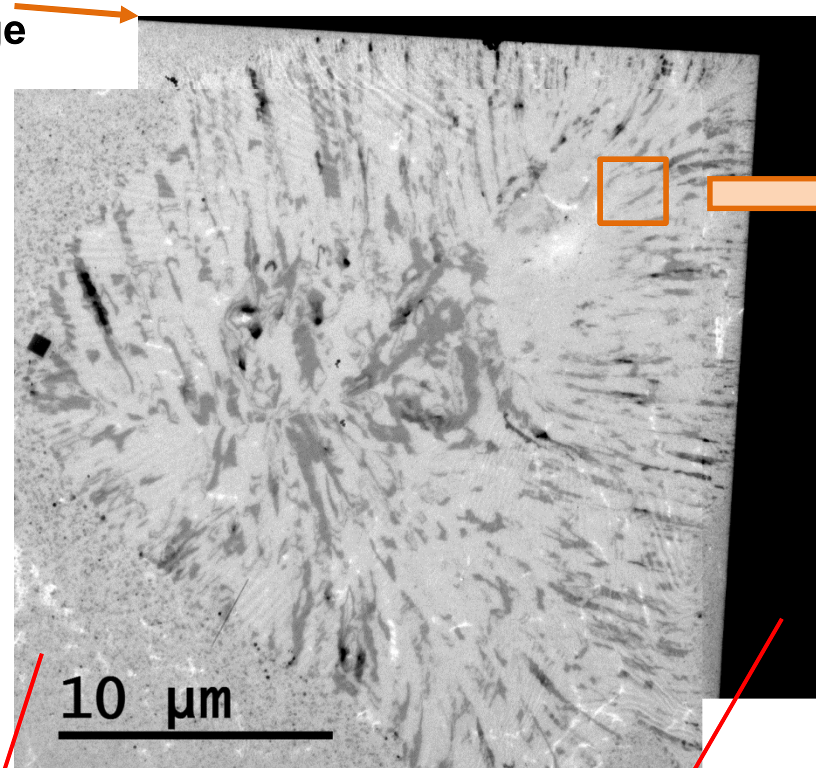




- Predicted cooling rate >> 1000 K/s
- Pre-heat TEM specimen during In-situ melting

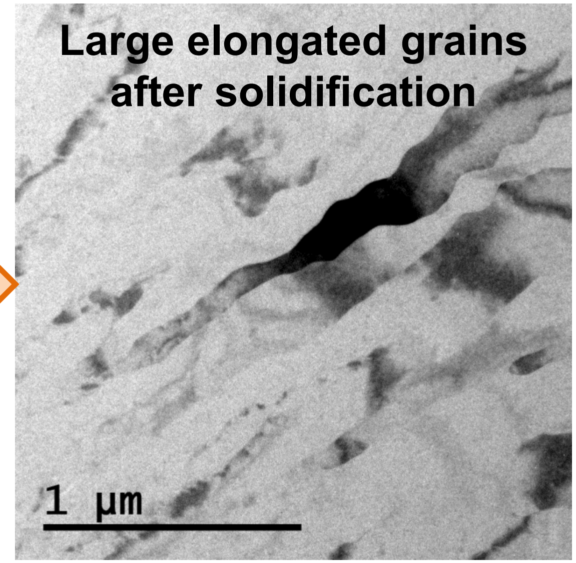
Technical Accomplishments:
Ex-situ Laser Melting Results

Si-window edge



Electron-transparent sputtered Mg-Al film

Electron-opaque Si chip



- Melting: 532 nm Nd:YAG pulsed laser, 0.35 mJ, 1µs pulse-length
- Work on DTEM on-going
- Incorporated Zn in the sputtered film → AZ91 film

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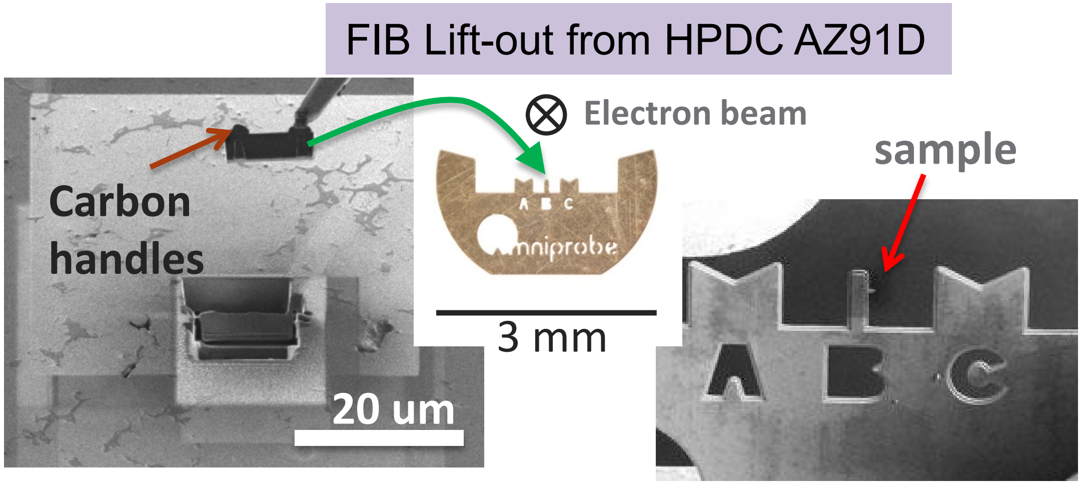
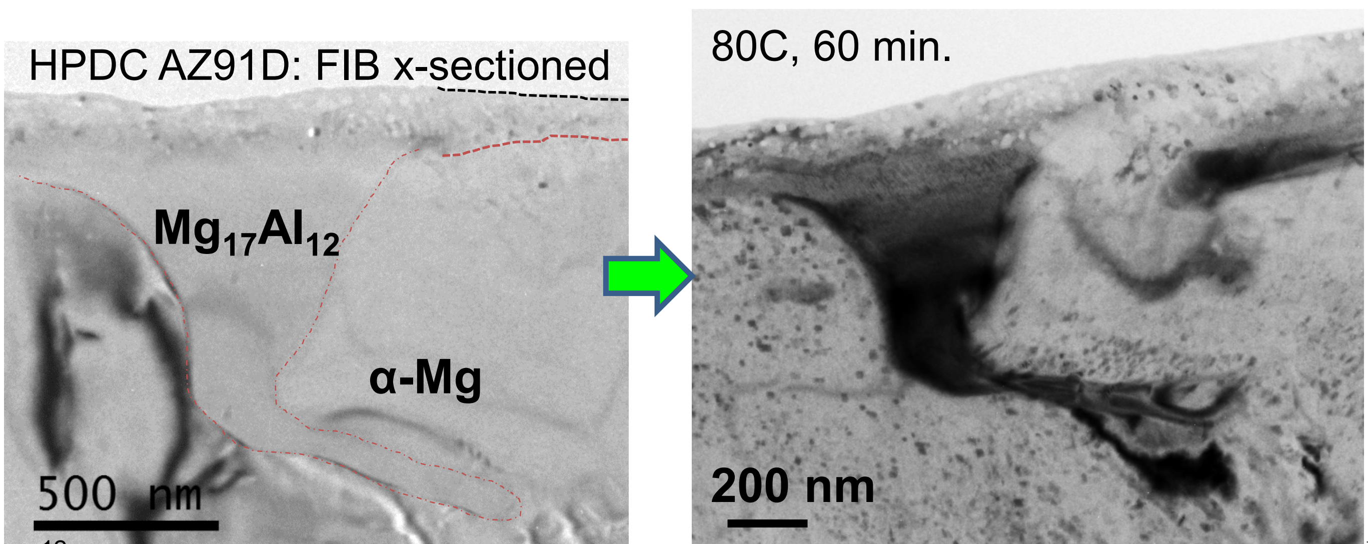
Technical Accomplishments:
In-situ Heat-treatment in STEM



- Initial plan: Use FIB to mill selected regions from as-cast AZ91 for heat-treatment
- Challenges with FIB:
  1. Use of Pt for sample manipulation catalyzes oxidation of Mg
  2. Use of Ga ions in FIB → Mg-Ga intermetallics during heat-treatment

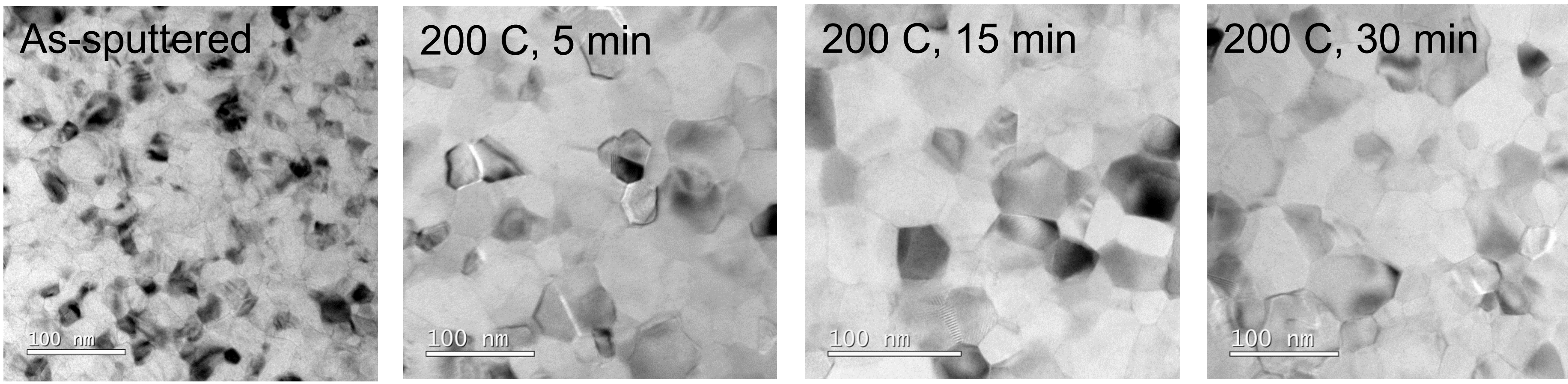


Current Approach

Use sputtered Mg-Al and Mg-Al-Zn (AZ91) films for heat-treatment

Technical Accomplishments:
Microstructure Evolution (STEM)

Grain size evolution in Mg-9 wt.% Al films (TEM Bright Field)



$$D^n - D_o^n = Kt$$
$$K = K_o \exp(-Q/RT)$$

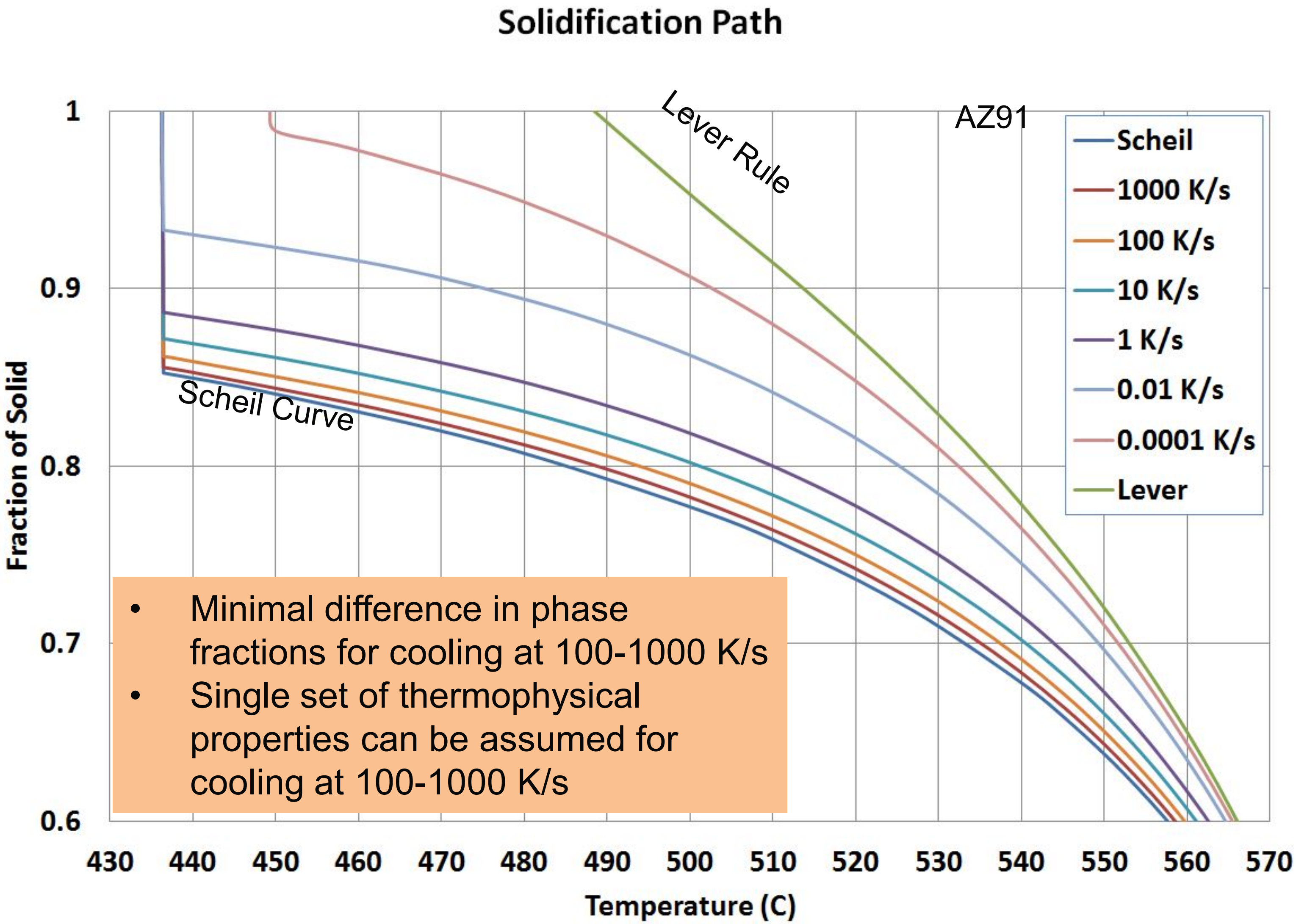
D: Size of α or $Mg_{17}Al_{12}$
Do: Initial size
n: Growth exponent
K: Growth constant
t: Time
T: Temperature

Results

n: Growth exponent vs. temperature
Q: Activation energy for growth

Technical Accomplishments:

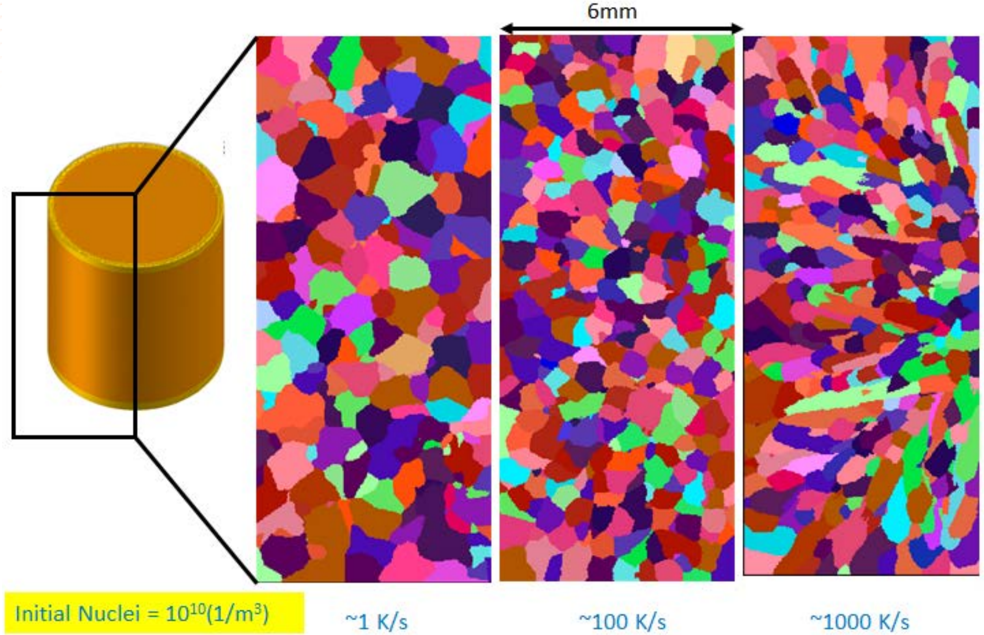
Solidification Modeling



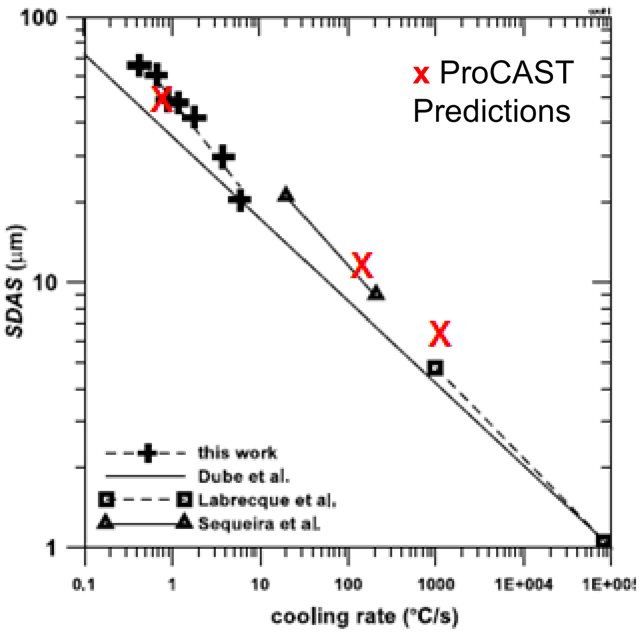
- Minimal difference in phase fractions for cooling at 100-1000 K/s
- Single set of thermophysical properties can be assumed for cooling at 100-1000 K/s

Technical Accomplishments:
ProCAST Predictions

Cellular Automata – Finite Element (CAFE) for grain prediction



SDAS Predictions



Caceres et al., Materials Science & Engineering A325(2002) 344-355

- Calibrated nucleation site density to match experimental grain-sizes and SDAS for different cooling rates

Technical Accomplishments: Atomistic Modeling

- Tested two modified Embedded Atom Method (MEAM) potentials

Potential 1: *Al/Si/Mg/Cu/Fe (Binary) MEAM Potential* (available from NIST)

B. Jelinek, S. Groh, M. F. Horstemeyer, J. Houze, S. G. Kim, G. J. Wagner, A. Moitra and M. I. Baskes, Phys Rev B **85**, 245102 (2012)

Potential 2: *Al-Mg Potential*

Y.-M. Kim *N. J. Kim, B.-J. Lee, CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 33 (2009) 650–657*

-Potential 1 gave properties (for $Mg_{17}Al_{12}$) that didn't match literature data

- *negative elastic constants c44, c55, c66*
- *+ve heat of formation*
- *-ve formation energy (substitutional atom)*

-We modified various parameters of Potential 2 to get physical properties of Mg, Al, Mg-Al and $Mg_{17}Al_{12}$ close to DFT/experimental values

Technical Accomplishments:

Atomistic Modeling ($Mg_{17}Al_{12}$ Properties)

Property	[2]	PNNL MEAM	[3]	DFT [3, 6]	Experimental [3]
Heat of Formation (meV/atom)	-44.2	-33.90	49.40	-17.0 – -48.0	-32.65 – -34.10
Cohesive energy (eV/atom)	-2.254	-2.33	-2.22	-2.03 – -2.47	Not Available
Lattice Constant (Å)	10.41	10.56	10.73	10.54 – 10.55	10.54 –10.56
Atomic Volume ($Å^3$)	19.45	20.31	21.28	18.65 –20.25	20.13 – 20.30
Bulk Modulus (GPa)	70.32	50.25	48.29	49.53 – 50.1	49.6

Good correlation with DFT and reported experimental values

[2] POSTEC CMSE LAB. https://cmse.postech.ac.kr/lammps/3707. Accessed June 10, 2014.

[3] Jelinek, B.; *et al* “Modified Embedded Atom Method Potential for Al, Si, Mg, Cu, and Fe Alloys.” *Phys Rev B* (85), 2012; pp. 245102.

[6] Kim, Y.-M.; *et al*. “Atomistic Modeling of Pure Mg and Mg–Al Systems. ” *CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry* (33), 2009; pp. 650–657.

Technical Accomplishments:
Atomistic Modeling (Elastic Properties)

Material	Al		Mg		$Mg_{17}Al_{12}$	
(GPa)	MEAM	Experimental [7]	MEAM	Experimental [7]	MEAM	DFT [8]
C_{11}	114.33	107.3	62.81	59.7	83.364	86.8
C_{22}	114.33	107.3	62.81	59.7	83.364	86.8
C_{33}	114.33	107.3	69.61	61.7	83.364	86.8
C_{12}	61.91	60.9	25.97	26.2	32.142	29.0
C_{13}	61.91	60.9	21.18	21.7	32.142	29.0
C_{23}	61.91	60.9	21.18	21.7	32.142	29.0
C_{44}	31.56	28.3	17.14	16.4	14.005	20.0
C_{55}	31.56	28.3	17.14	16.4	14.005	20.0
C_{66}	31.56	28.3	18.42	Not Listed	14.005	20.0

- Existing precipitation models assume elastic constants of $Mg_{17}Al_{12}$ = Mg
- Good correlation with experimental values of Mg & Al, and DFT values of $Mg_{17}Al_{12}$

[7] Simmons, G.; Wang, H. *Single Crystal Elastic Constants and Calculated Aggregate Properties. A Handbook*. MIT Press Cambridge, Mass., 1971.

[8] Wang, N. *et al*. “Structural and Mechanical Properties of $Mg_{17}A_{l2}$ and $Mg_{24}Y_5$ from First-principles Calculations.” *J. Phys. D. Appl. Phys.* (41), 2008; pp. 195408.

Response to Reviewers' Comments

- 1st year for review

Collaboration

- ESI North America (sub-contract)
  - Solidification modeling
  - Thermal modeling of in-situ melting and solidification

Remaining Challenges & Barriers

<u>Challenge</u>

- DTEM up and running
  - Optimize imaging conditions (signal-to-noise)
- Reduce the in-situ cooling rate (100-1000 ºC/s)

<u>Barrier</u>

- Inability to measure temperature inside the DTEM

Proposed Future Work:
Upcoming Project Work

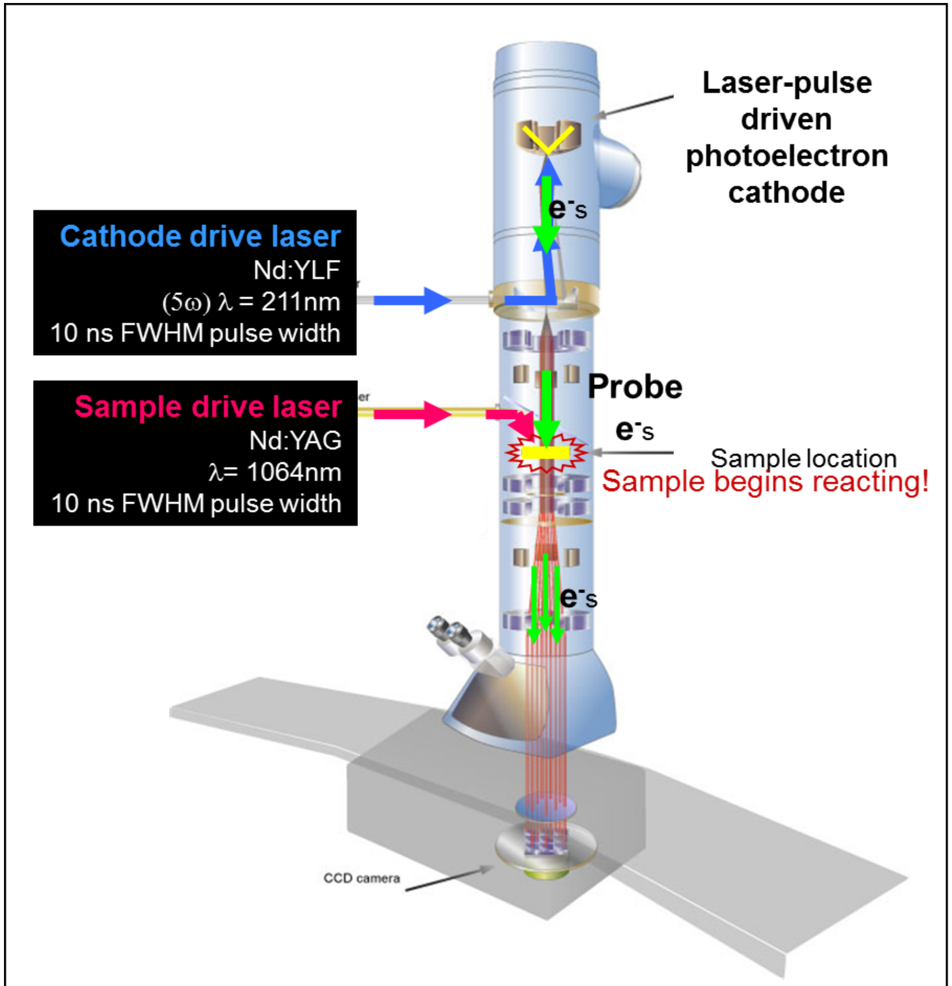
- Perform DTEM experiments
- Solidification modeling
  - Use in-situ DTEM data for modeling
- Heat-treatment
  - Determine grain growth kinetics and study effects of Zn (binary vs. ternary films)
- Atomistic modeling
  - Determine diffusion coefficients and effective migration barriers as a function of Al concentration and temperature

Summary

- The goal is to understand the kinetics & diffusion in Mg alloys under non-equilibrium conditions → AZ91 as a model system
- Ex-situ laser melting/solidification experiments and their thermal modeling has been completed → Work on in-situ melting/solidification in a dynamic TEM is in progress
- FIB-based technique for specimen extraction from bulk AZ91 alloy poses unique challenges for in-situ heat-treatment in TEM → Sputtered films are being used to study microstructural evolution during heat-treatment
- ProCAST calibration parameters for SDAS and grain-size in AZ91 have been determined. → Goal is to compare in-situ solidification results with ProCAST predictions
- Atomistic modeling has improved upon existing Mg-Al potential to predict $Mg_{17}Al_{12}$ properties → Kinetic Monte Carlo method is being used to simulate microstructural evolution of heat-treated sputtered films

Technical Back-Up Slides

Background:
Dynamic Transmission Electron Microscope (DTEM)



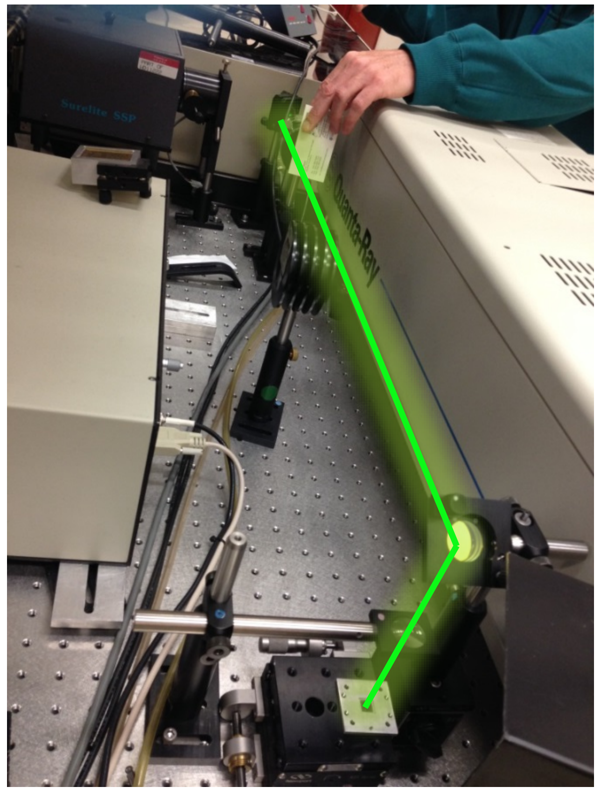
- Laser-driven photocathode electron source
- Resolution: ~0.3 nm, ~100 ns
- 2 separate lasers → wide range of time delays between the pump and the probe lasers
- The drive laser can be modified (bio-specimens as well)
- 2k x 2k CCD camera

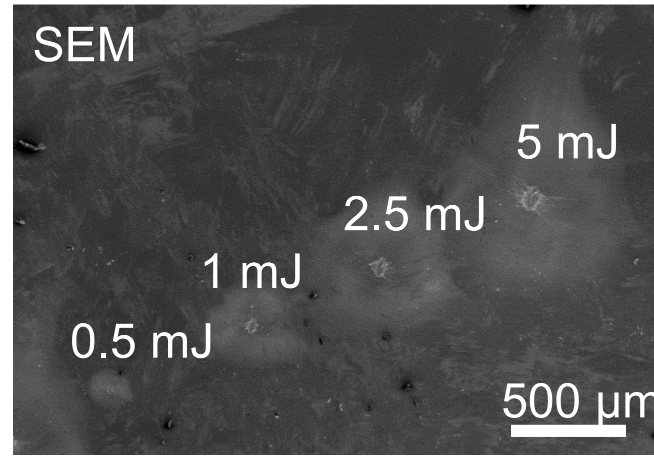
Challenges

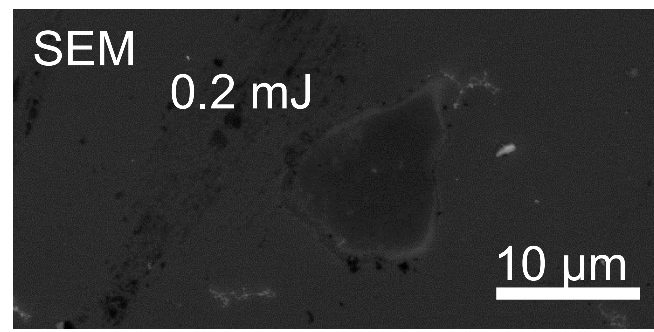
- Temperature control
- Cooling rate control
- Optimize imaging conditions

Technical Accomplishments:
Ex-situ Laser Melting Calibration

- Pulsed Nd:YAG laser (532 nm)
- Pulse length: 1 μs
- Single-shot mode
- Melt in ambient







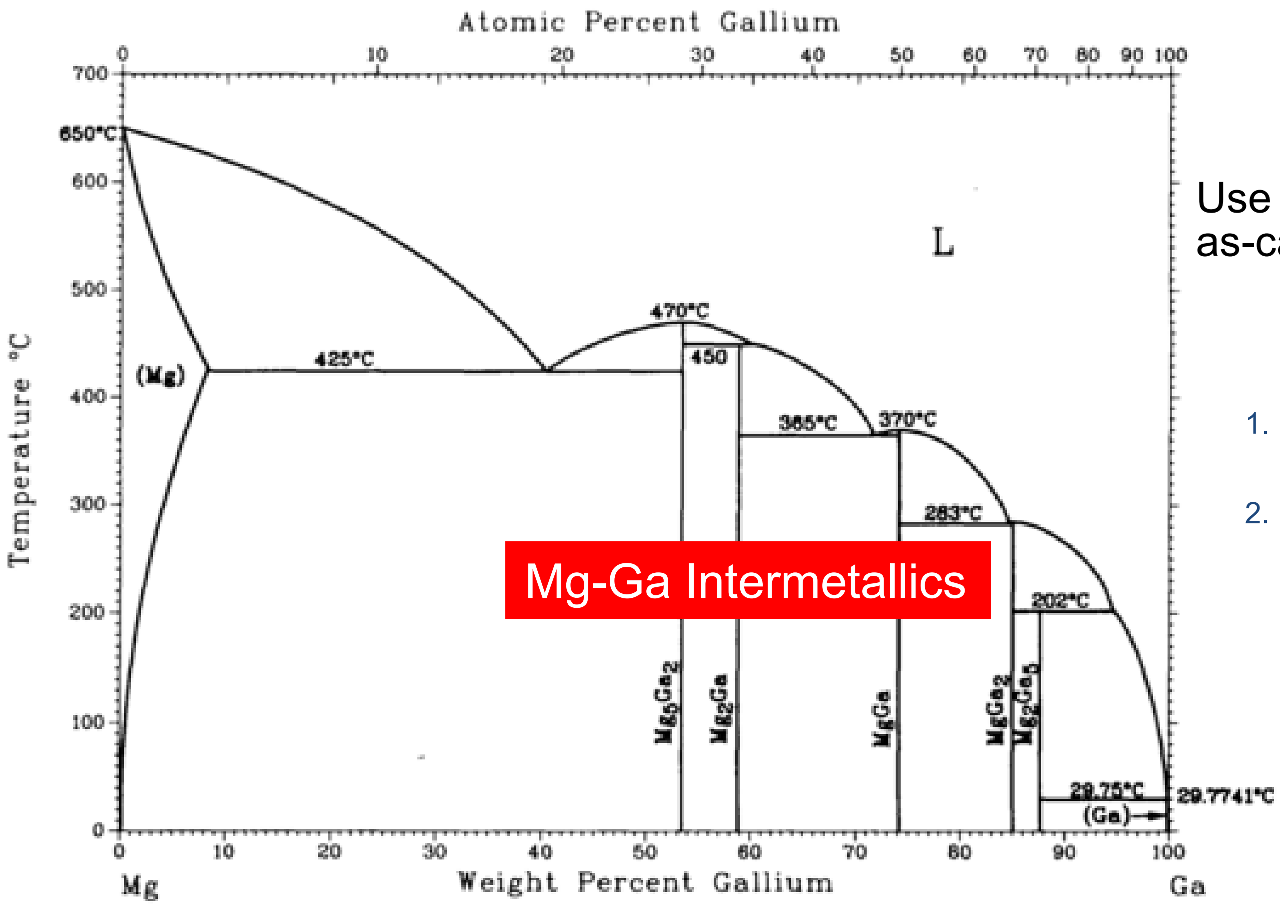
Laser-Melting Parameters

0.35 mJ energy
1μs pulse-length

Technical Issues:
In-situ Heat-treatment in STEM

Ga-Mg (Gallium - Magnesium)

H. Okamoto, 1991



Initial plan

Use FIB to mill selected regions from as-cast AZ91 for heat-treatment

Challenges with FIB

1. Use of Pt for sample manipulation catalyzes oxidation of Mg
2. Use of Ga ions in FIB → Mg-Ga intermetallics during heat-treatment

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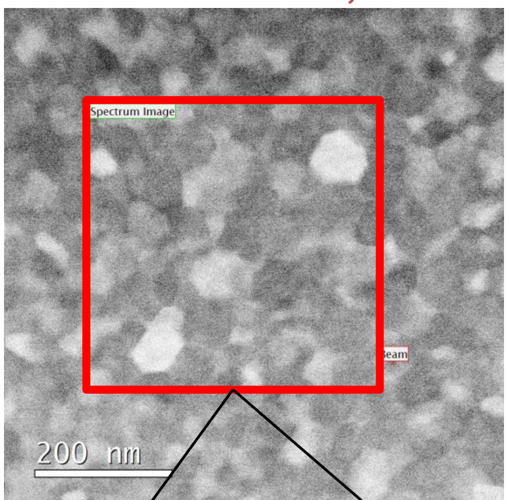
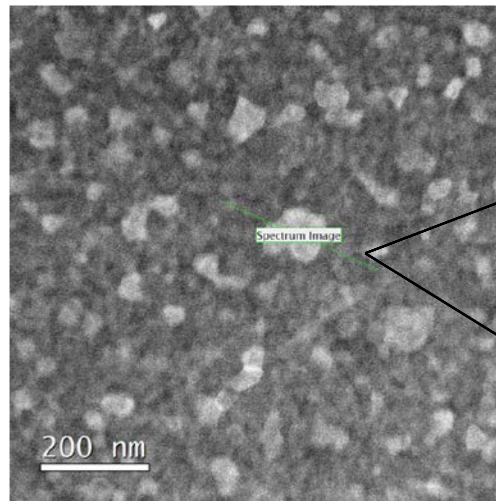
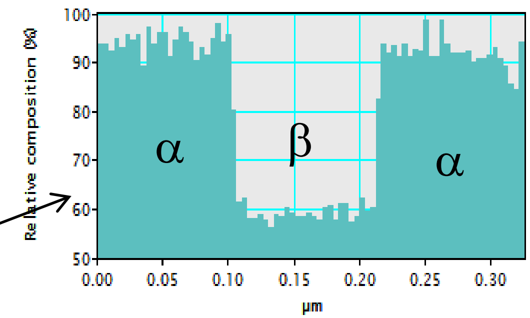
Technical Accomplishments:
Microstructure Evolution (STEM)

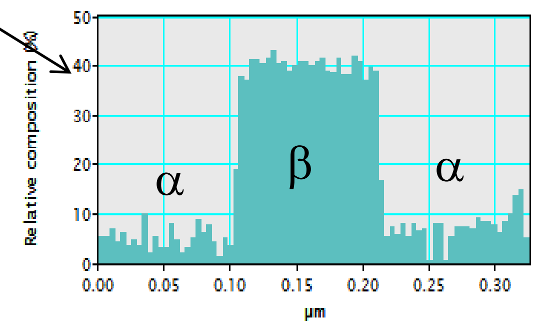
Phase evolution in Mg – 9Al thin film during heat treatment

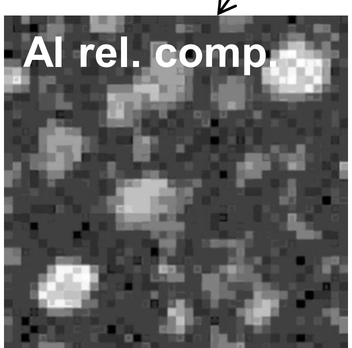
STEM ADF 300C, 30 min

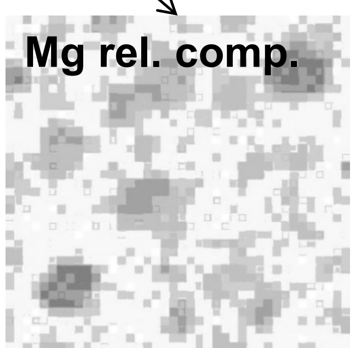


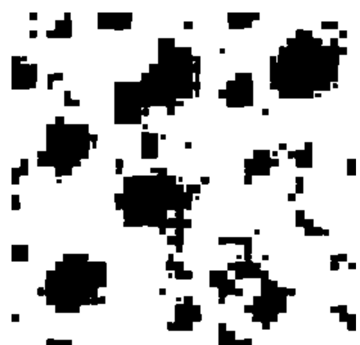












Threshold image → Image analysis for area fraction, size

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Technical Accomplishments:
Atomistic Modeling (Energy of Formation)

Material	Vacancy (eV)		Intersitial (eV)				Substitutional Atom (eV)			
			MEAM		DFT [3]		MEAM		DFT [3]	
	MEAM	DFT (Exp.) [3]	Octa.	Tetra.	Octa.	Tetra.	Mg	Al	Mg	Al
Al	0.68	0.55 (0.67)	2.65	3.11	2.8	3.3	0.04	-	0.05	-
Mg	0.89	0.7 (0.5-0.89)	2.54	2.57	2.2	2.2	-	0.013		0.06

PNNL adjusted MEAM gave values closer to published DFT/experimental values

[3] Jelinek, B.; *et al* “Modified Embedded Atom Method Potential for Al, Si, Mg, Cu, and Fe Alloys.” *Phys. Rev B* (85), 2012; pp. 245102.